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GROUND STATE POTENTIAL ENERGY

OF DIATOMIC MOLECULES

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ABSTRACT

The restrictions placed on the ground state potential energy of
a diatomic molecule by the inequality $d^2(R^2E)/dR^2 < 0$ are discussed.
This leads to rather weak smoothness conditions on $E(R)$.

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Introduction

Strictly speaking, a potential function for a molecule is purely
a theoretical intermediate in the approximate calculation of the
energy levels and not an experimental observable. There would seem
to be little reason, then, to speak of an "experimental" potential
function. On the other hand, it is impractical, if not impossible, to
compute with spectroscopic accuracy the theoretical potential functions
for all molecules of physical interest. Thus it is not surprising that
numerous methods have been developed for estimating the potential
function from experimental data. A good summary of these methods may
be found in the review article by Varshni.[1]

As no two of these methods yield the same potential function, it
is of some interest to know as much as possible about the theoretical
potential function itself. Again, Varshni has summarized several
basic conditions on the exact potential function. There are, however,
probably a wide variety of theorems which can be proven concerning
theoretical potential functions. Most of the theorems presented in
this paper take the form of inequalities which place rather weak
restrictions on the potential function.

Discussion

If $H_e(R)$ denotes a set of electronic Hamiltonians labeled by
the parameter R and $E_e(R)$ denotes the corresponding energy, then in
atomic units,

$$H_e = T_e + V_e \tag{1a}$$

where
$$T_e = -\frac{1}{2} \sum_{i=1}^{N} \nabla_i^2 \tag{1b}$$

$$V_e = \sum_i \frac{z_a}{r_{ai}} + \frac{z_b}{r_{bi}} + \sum_{i>j} \frac{1}{r_{ij}} \tag{1c}$$

and
$$H_e \psi = E_e \psi \tag{1d}$$

The potential function $E(R)$ is then given by

$$E(R) = E_e(R) + z_a z_b / R \ .. \tag{1e}$$

From the fact that T_e and V_e are homogeneous functions of the unit of length, it follows that $\partial T_e / \partial R = -2T_e / R$ and $\partial V_e / \partial R = -V_e / R$. This yields the well known equations[2],

$$R \, \partial H_e / \partial R = -2T_e - V_e \tag{2a}$$

$$-T_e = R \partial H_e / \partial R + H_e = \partial (RH_e) / \partial R \tag{2b}$$

$$V_e = R \partial H_e / \partial R + 2H_e = R^{-1} \partial (R^2 H_e) / \partial R. \tag{2c}$$

Another relationship which is not so well known, can be found from

$$R^2 \partial^2 H_e / \partial R^2 = 6T_e + 2V_e$$

by substituting for T_e and V_e to obtain

$$R^2 \partial^2 H_e / \partial R^2 + 4R \partial H_e / \partial R + 2H_e = 0 \tag{3}$$

If the symbol $|E_e R\rangle$ is used to denote an eigenstate of $H_e(R)$, then $E_e^{\ o}(R) = \langle E_e^{\ o}R \mid H_e \mid E_e^{\ o}R\rangle$ where $E_e^{\ o}$ is the lowest eigenvalue of H_e. Since $H_e(R)$ has no singularities in R, it may be expanded in the form

$$H_e(R_1) = H_e(R) + (R_1 - R) \, \partial H_e(R)/\partial R + \frac{1}{2}(R_1 - R)^2 \, \partial^2 H_e(R)/\partial R^2 + O(R_1 - R)^3.$$

By perturbation theory it follows at once that,[6]

$$\lim_{R_1 \to R} E_e^{\ o}(R_1) = E_e^{\ o}(R) \tag{5a}$$

$$\lim_{R_1 \to R} dE_e^{\ o}(R_1)/dR_1 \equiv dE_e^{\ o}(R)/dR = \langle E_e^{\ o}R \mid \partial H_e/\partial R \mid E_e^{\ o}R\rangle \tag{5b}$$

$$\lim_{R_1 \to R} d^2 E_e^{\ o}(R_1)/dR_1^{\ 2} \equiv d^2 E_e^{\ o}(R)/dR^2 = \langle E_e^{\ o}R \mid \partial^2 H_e/\partial R^2 \mid E_e^{\ o}R\rangle - 2R^{-2} f(R) \tag{5c}$$

$$\text{where} \quad f(R) = R^2 \sum_{E_e > E_e^{\ o}} \frac{|\langle E_e^{\ o}R \mid \partial H_e/\partial R \mid E_e R\rangle|^2}{E_e - E_e^{\ o}} > 0. \tag{6a}$$

The formula for $f(R)$ can be simplified by equation (2a) to

$$f(R) = \sum_{E_e > E_e^{\ o}} \frac{|\langle E_e^{\ o}R \mid T_e \mid E_e R\rangle|^2}{E_e - E_e^{\ o}} = \sum_{E_e > E_e^{\ o}} \frac{|\langle E_e^{\ o}R \mid V_e \mid E_e R\rangle|^2}{E_e - E_e^{\ o}}. \tag{6b}$$

Since the coordinate transformations which commute with H_e also commute with V_e and T_e separately, it follows that the sum over $E_e > E_e^{\ o}$ really only extends over states of the same symmetry as the ground state.

Equation (5a) is, of course, the Hellman-Feynman theorem $dE_e/dR = \langle \partial H_e/\partial R\rangle$. Equation (5b) leads to the conclusion that $d^2 E_e/dR^2 < \langle \partial^2 H_e/\partial R^2\rangle$ for the ground state where the bracket denotes the average value.

A result similar to this can be obtained for an optimized para-meter wave function[3] $\phi(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N, a_1 \ldots a_M)$ where the a_i are variational parameters and ϕ has no explicit R dependence. If $\bar{E} = (\phi, H\phi) / (\phi, \phi)$, then by an optimized wave function it is meant that $\partial \bar{E}/\partial a_i = 0$ for all i and R. But

$$d\bar{E}/dR = (\partial \bar{E}/\partial R)_{a_1 \ldots a_m} + \sum_{i=1}^{M} (da_i/dR)(\partial \bar{E}/\partial a_i) \tag{7a}$$

and

$$\frac{d^2\bar{E}}{dR^2} = \frac{d}{dR}\left(\frac{\partial \bar{E}}{\partial R}\right) + \frac{d}{dR}\left[\sum_i \left(\frac{da_i}{dR}\right)\left(\frac{\partial \bar{E}}{\partial a_i}\right)\right] \tag{7b}$$

Since

$$\frac{d}{dR}\left(\frac{\partial \bar{E}}{\partial R}\right) = \frac{\partial^2 \bar{E}}{\partial R^2} + \sum_i \left(\frac{da_i}{dR}\right)\frac{\partial}{\partial a_i}\left(\frac{\partial \bar{E}}{\partial R}\right)$$

it follows from equation (7a) and $\partial \bar{E}/\partial a_i = 0$ that

$$\frac{d}{dR}\left(\frac{\partial \bar{E}}{\partial R}\right) = \frac{\partial^2 \bar{E}}{\partial R^2} - \sum_{i,j} \left(\frac{da_i}{dR}\right)\left(\frac{da_j}{dR}\right)\frac{\partial^2 \bar{E}}{\partial a_i \partial a_j} \tag{8}$$

Equation (7b) then becomes

$$\frac{d^2\bar{E}}{dR^2} = \frac{\partial^2 \bar{E}}{\partial R^2} - \sum_{i,j} \left(\frac{da_i}{dR}\right)\left(\frac{da_j}{dR}\right)\frac{\partial^2 \bar{E}}{\partial a_i \partial a_j} \tag{9}$$

But the condition that $\bar{E}$ be a minimum with respect to all the a_i is precisely that the quadratic form

$$\sum_{i,j} x_i x_j \frac{\partial^2 \bar{E}}{\partial a_i \partial a_j}$$

be positive definite. Hence it follows that

$$\frac{d^2 \bar{E}}{dR^2} < \left(\frac{\partial^2 \bar{E}}{\partial R^2}\right)_{a_1 \ldots a_m} .$$

Thus for either an optimized approximate solution or an exact solution there is an inequality of the form,

$$d^2 E_e / dR^2 < \left\langle \partial^2 H_e / \partial R^2 \right\rangle \quad . \tag{10}$$

If the expression from equation (3) is substituted for $\partial^2 H_e / \partial R^2$, this inequality becomes $d^2(R^2 E_e)/dR^2 < 0$, or in the case of the exact energy $d^2(R^2 E_e)/dR^2 = -2f(R)$. Another inequality is readily obtained from the fact that $\bar{T}_e$ is positive. Hence the inequalities

$$d^2(R^2 E)/dR^2 \eqsim d^2(R^2 E_e)/dR^2 < 0 \tag{11a}$$

$$d (RE)/dR \eqsim d (RE_e)/dR < 0 \tag{11b}$$

$$E - z_a z_b/R \eqsim E_e < 0 \tag{11c}$$

must be satisfied by the ground state potential energy of every dia-tomic molecule.

The first of these inequalities places a restriction on the force constant of the form,

$$r_e^2 k_e < - 2 E(r_e) \tag{12}$$

Since the zero of energy is fixed by equation (1) at the energy of the system when each electron and nucleus is isolated from all others, this inequality is much too weak to be useful. It is interesting to note, however, that Sutherland[4] has found a closely related quantity, $r_e^2 k_e / D_e$, to be approximately constant within the same class of molecules. The second inequality merely restricts the slope dE/dR

since it implies $R \, dE/dR < - E$.

The importance of the inequalities (11) lies in their implications concerning the smoothness of $E(R)$. Integration of these inequalities shows that RE, $R^2 E_e$, and $d(R^2 E)/dR$ must all be monotonic decreasing functions of R. Also, $R^2 E$ is monotonic increasing to a positive maximum and monotonic decreasing beyond this maximum.

Repeated integration of inequality (11a) yields the inequality

$$\frac{R_4^2 E(R_4) - R_3^2 E(R_3)}{R_4 - R_3} \leqslant \frac{R_2^2 E(R_2) - R_1^2 E(R_1)}{R_2 - R_1} \quad \text{for } R_4 \geqslant R_3 \geqslant R_2 \geqslant R_1 . \quad (13a)$$

This should be a useful checking formula for an empirical potential function if the four points are closely spaced. For $R_3 = R_2 = R$ this may be written as

$$\frac{1}{R^2} \left\{ \frac{R_4 R_1 \left[R_1 E(R_1) - R_4 E(R_4) \right]}{R_4 - R_1} \right\} = \frac{1}{R} \left\{ \frac{R_1^2 E(R_1) - R_4^2 E(R_4)}{(R_4 - R_1)} \right\} \leqslant E(R)$$

$$\text{for } R_4 \geqslant R \geqslant R_1 \quad (13b)$$

This states that a Fues potential[5], $\frac{a}{R^2} - \frac{b}{R}$, which is correct for two values of R will be too low for intermediate values of R.

Double integration of $d^2(R^2 E)/dR^2 = -2f(R)$ yields

$$R_1^2 E(R_1) = R^2 E(R) + (R_1 - R) \left[2RE(R) + R^2 dE(R)/dR \right] - (R_1 - R)^2 f(\zeta)$$

$$\text{for } R_1 \geqslant \zeta \geqslant R \quad (14)$$

Some properties of the function $f(R)$ can be obtained from the limiting values of $d^2(R^2 E)/dR^2$. For instance,

$$\lim_{R \to \infty} d^2(R^2 E e)/dR^2 = 2E_e(\infty) = -2f(\infty).$$

Thus, $f(\infty)$ is the negative of the energy of the separated atoms. Also,

$$\lim_{R \to 0} d^2(R^2 E_e)/dR^2 = 2E_e(0) = -2f(0).$$

So $f(0)$ is the absolute value of the energy of the united atom. This gives the interesting theorem,

$$E_a^{\,0} = -\sum_{E_a > E_a^{\,0}} \frac{|\langle E_a | V_a | E_a^{\,0}\rangle|^2}{E_a - E_a^{\,0}} = -\sum_{E_a > E_a^{\,0}} \frac{|\langle E_a | T_a | E_a^{\,0}\rangle|^2}{E_a - E_a^{\,0}} \tag{15}$$

where T_a and V_a are the kinetic and potential energy operators for an atom and the $|E_a\rangle$ are the energy eigenstates of that atom. It also follows from this that

$$-E_a^{\,0}(E_a^{\,1} - E_a^{\,0}) \leqslant \langle E_a^{\,0} | V_a^{\,2} | E_a^{\,0}\rangle - \langle E_a^{\,0} | V_a | E_a^{\,0}\rangle^2 \tag{16a}$$

and

$$-E_a^{\,0}(E_a^{\,1} - E_a^{\,0}) \leqslant \langle E_a^{\,0} | T_a^{\,2} | E_a^{\,0}\rangle - \langle E_a^{\,0} | T_a | E_a^{\,0}\rangle^2 \tag{16b}$$

which gives a lower bound to the mean square deviation of T_a and V_a for an atom in its ground state.

It is clear from this that $f(R)$ is rather large. In fact, for the hydrogen molecule in Hartree atomic units,

$$f(0) = 2.904 , \quad f(r_e) = 0.808 , \quad f(\infty) = 1 .$$

For other molecules $f(R)$ can be expected to be even larger. Hence the last term in equation (14) cannot be neglected unler $(R_1 - R)^2$ is small compared to $(R_1 - R)$.

If the inequality (11a) is written in the form

$$2 \frac{d}{dR}(RE) + R \frac{d}{dR}\left[\frac{d}{dR}(RE)\right] < 0$$

and equation (2b) is substituted, the inequality

$$d \, \overline{T}_e / \, dR \, > \, - \, 2 \, \overline{T}_e / R$$

is obtained. Or in a different form,

$$d \, \overline{T}_e / dR - \langle dT_e / dR \rangle \; = \; -R^{-1} \, d^2(R^2 E) / dR^2 \; > \; 0 \qquad (17a)$$

$$d \, \overline{V} / dR \; - \; \langle dV / dR \rangle \; = \; +R^{-1} \, d^2(R^2 E) / dR^2 \; < \; 0 \qquad (17b)$$

Thus it is seen that dE/dR is obtained correctly from $\langle dH/dR \rangle$ because $d\overline{T}/dR$ has been underestimated by the same amount that $d\overline{V}/dR$ has been overestimated.

Since the derivation of the inequalities (11) holds equally well for the lowest excited state of each symmetry it follows that the inequalities (12), (13), (14) and (17) apply to the potential curves for these states also. If, in equations (15) and (16), $E_a^{\,o}$ and $E_a^{\,1}$ are interpreted to mean the first two energy levels of a given symmetry, equations (15) and (16) can also be applied to excited states.

Conclusion

The inequality $d^2(R^2 E)/dR^2 < 0$ places certain rather weak restrictions on the form of the potential curve for the ground state of a diatomic molecule. These restrictions probably do not justify the amount of smoothness usually assumed in constructing an approximate potential curve by empirical methods but they do imply that the exact potential curve is not too badly behaved.

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